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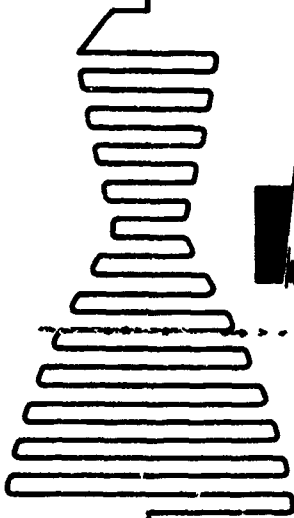
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R-8037

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(Unclassified Report)

SEMIANNUAL REPORT,
INORGANIC HALOGEN OXIDIZERS

(1 April 1969 through 30 September 1969)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

Contract Nonr 4428(00)
G.O. 8614

Office of Naval Research
Power Branch
Code 429

PREPARED BY

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Oxidizer and Fluorine Chemistry Group

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NO. OF PAGES 34 & vi

REVISIONS

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FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Navy Contract Nonr 4428(00) and covers the period 1 April 1969 through 30 September 1969. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in the Oxidizer and Fluorine Chemistry Group with Dr. D. Pilipovich as Responsible Scientist. Staff Members contributing to the technical effort include Dr. D. Pilipovich, Dr. C. J. Schack, Dr. K. O. Christe, Dr. E. C. Curtis, Dr. C. B. Lindahl, and Mr. R. D. Wilson.

ABSTRACT

The new compound chlorine perchlorate, Cl_2O_4 , was synthesized from the action of chlorine fluorosulfate on several perchlorate salts. Characterization data, physical and chemical properties are described. The use of N_2O as an oxygen source for the synthesis of ClF_3O was successful but offered no advantages over oxygen. A new synthesis of nitryl chloride emerged from the studies of $\text{Ca}(\text{OCl})_2$ as an intermediate and involved the action of nitrosyl fluoride, FNO , on calcium hypochlorite. A structural evaluation on chlorine fluorosulfate was carried out from its ir spectrum. C_s symmetry for ClSO_3F was suggested and thermodynamic properties and force constants were computed.

(Confidential Abstract)

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INTRODUCTION

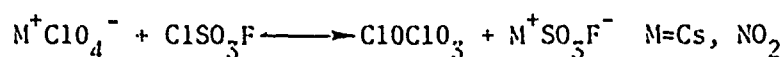
The program to be reported herein constitutes a continuation of a basic synthesis program in the area of inorganic halogen oxidizers. In the main, the program had been devoted to halogen fluorides, oxyfluorides and derivatives of both. During the past period, however, we have augmented our fluorine research with studies in the halogen oxide area. Specifically, a multifaceted program was begun in (1) studying the synthesis of halogen oxides through positive halogenation reaction, (2) evaluating positive halogenation reagents, and (3) assessing the reaction chemistry of all intermediates in synthesizing new, energetic materials. This report describes the work in preparing the new chlorine oxide, chlorine perchlorate, its characterization, and some of its reaction chemistry.

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DISCUSSION

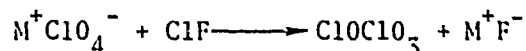
CHLORINE PERCHLORATE--PREPARATION AND PROPERTIES

In the course of developing the synthesis of chlorine fluorosulfate, ClSO_3F , from ClF and SO_3 (Ref. 1) it was observed that this material exhibits an unusual degree of reactivity as a "positive" chlorinating agent. Efforts to take advantage of this property were made by attempting the chlorination of perchlorate anions.



The unusual new chlorine oxide sought through this reaction was produced in high yield (75 to 95 percent) at a temperature of approximately -45 C. This oxide, chlorine perchlorate, is unusual as it represents the first example of a stable Cl-O compound containing chlorine in two different valence states.

Chlorine perchlorate had been the goal of an earlier reaction of this type in which chlorine monofluoride was used as the source of positive chlorine (Ref. 2).



Yields from these reactions were low and irreproducible inhibiting a conclusive identification of the product, but comparison of infrared data has shown that ClOClO_3 had been formed by the ClF reaction also.

The identification and physical characterization of chlorine perchlorate has been completed. Full details of this work is set forth in Appendix A of this report. Four reasonably stable oxides of chlorine are known and the properties of these are summarized in Table 1 as reviewed by Schmeisser

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TABLE 1

PHYSICAL PROPERTIES OF THE OXIDES OF CHLORINE

| Oxide Property | Cl ₂ O | ClO ₂ | Cl ₂ O ₆ | Cl ₂ O ₇ | ClOClO ₃ |
|---------------------------------|-------------------|------------------|--------------------------------|--------------------------------|---------------------|
| Molecular Weight | 87 | 67.5 | 167 | 183 | 135 |
| Melting Point, C | -116 | -59 | 3.5 | -91.5 | -117 |
| Boiling Point, C | 2.0 | 11.0 | 203 (calc) | 80 | 45.5 |
| Vapor Pressure at 0 C | 699 | 490 | 0.31 | 23.7 | 119 |
| log P _{mm} | 7.87-1373/T | | 7.1-2070/T | 8.03-1818/T | 7.8156-1568.0/T |
| Trouton's Constant | 22.5 | 23.0 | 21 | 23.4 | 22.6 |
| Heat of Vaporization, kcal/mole | 6.20 | 6.52 | 9.5 | 8.29 | 7.17 |
| Heat of Formation, kcal/mole | 21.0 | 25 | | 63.4 | 43 |
| Density, gm/cc | * | 1.64 at 0 C | 2.02 at 3.5 C | 1.86 at 0 C | 1.82 at 0 C |
| Liquid Color | Red-brown | Red-brown | Deep red | Colorless | Pale yellow |

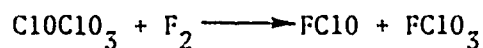
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and Brandle (Ref. 3). Supplemental data have been added and the properties of ClOClO_3 are noted for comparison. Recently, a fifth oxide of chlorine has been reported (Ref. 4) with the empirical formula $\text{ClO}_{1.5}$ and the postulated composition OClClO_2 . This compound is only marginally stable at -45°C and is very explosive (Ref. 4 and 5).

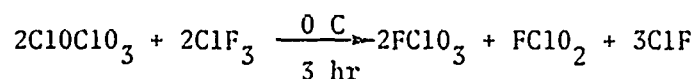
REACTIONS OF CHLORINE PERCHLORATE

In addition to the reactions of chlorine perchlorate given in Appendix A, some other reactions have been examined. The fluorination of ClOClO_3 was of particular interest. It was anticipated that this reaction would probably proceed by either of the following paths:



Chlorine oxide fluoride, FClO , would not necessarily be found as such because its further fluorination to Florox, ClF_3O , might occur readily. Using excesses of fluorine, it was observed that little or no reaction occurred at -78°C or -45°C despite long reaction periods (18 and 9 days). At 0°C , however, complete consumption of the ClOClO_3 was noted in 3 days. The products were FClO_3 , FClO_2 , and ClF . Neither fluorine perchlorate nor Florox were obtained. The conditions required for reaction and the products formed indicate that dissociation or decomposition of ClOClO_3 may be necessary before fluorination can occur. Behavior of this type has been reported (Ref. 6) for the reaction of F_2 with Cl_2O_6 .

Chlorine perchlorate and chlorine trifluoride reacted smoothly and at a moderate rate. The consumed starting materials and the products formed agreed well with the overall stoichiometry shown:

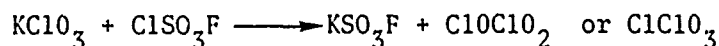


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The total absence of fluorine perchlorate and the near quantitative oxygen material balance (as FClO_3 and FClO_2) indicates that fluorination of either atom of the terminal Cl-O bond did not occur. Instead, fluorination of the central chlorine atom to give FClO_3 appears certain. The remaining products would arise by disproportionation of the ClO species either before or after fluorination.

ATTEMPTED SYNTHESIS OF CHLORINE CHLORATE

Extension of the reaction of ClSO_3F to other chlorine oxide anions offers a potential route to other new chlorine oxides. An initial effort in this direction was made through the following reaction:



Either of two structural compositions might result from this reaction and neither is the same as that postulated (Ref. 4) for the aforementioned explosive chlorine oxide of this same empirical formula, Cl_2O_3 . When the above reaction was conducted at -45°C , only Cl_2 , ClO_2 , and O_2 were observed, indicating that the isomer, ClOClO_2 , may have formed but decomposed. The alternate isomer would be expected to give Cl_2 and Cl_2O_6 upon decomposition. Further attempts to synthesize chlorine chlorate, using lower temperatures and other salts, are in progress.

ATTEMPTED SYNTHESIS OF NEW COVALENT HYPOCHLORITES

A convenient synthesis of chlorine nitrate was discovered (Ref. 7) through the reaction of $\text{Ca}(\text{OCl})_2$ and NO_2F :

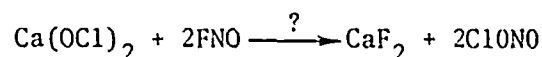


The reaction was most successful at low temperatures ($T < 0$) and the ease of reaction suggested that calcium hypochlorite may be converted to other covalent hypochlorites.

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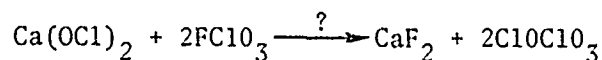
One of the more intriguing possibilities was the use of $\text{Ca}(\text{OCl})_2$ in synthesizing the unknown chlorine nitrite, ClONO :



We examined the reaction under a variety of conditions and found that instead of ClONO the isomeric nitryl chloride, ClNO_2 , was produced. Yields of ClNO_2 noted were 2 percent at ambient temperature, 39 percent at -112°C , 78 percent at -126°C , and 52 percent at -142°C .

The workup of all of the above reactions involved a warmup to ambient temperature prior to fractionation and ir examination. We considered the possibility that ClONO , if formed, could rearrange during the warmup period. In order to test this thesis, low-temperature ir spectra were recorded on samples which were not warmed above -78°C . These spectra showed no peaks different than those exhibited by solid ClNO_2 under the same conditions. Thus, ClONO appears not to have formed at all. However, the process does offer a convenient synthesis of nitryl chloride because FNO can be made conveniently from CsF and N_2O_4 (Ref. 8).

Several attempts were made to prepare new chlorine oxides from $\text{Ca}(\text{OCl})_2$. The reaction of ClF with $\text{Ca}(\text{OCl})_2$ was anticipated to yield Cl_2O and, indeed, did so at -112°C . The less reactive perchloryl fluoride, FClO_3 , was then reacted with the hope that a new route to ClOClO_3 could evolve:



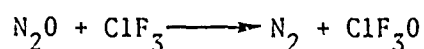
Not surprisingly, FClO_3 did not react with $\text{Ca}(\text{OCl})_2$ at temperatures up to 100°C . Additional reactions will be studied using $\text{Ca}(\text{OCl})_2$ and it is anticipated that new mixed halogen oxides are highly probable as products.

PHOTOCHEMICAL SYNTHESIS OF FLOROX

The synthesis of ClF_3O through uv activation has been accomplished in excellent yield with a variety of reactant systems (Ref. 1 and 2) under a variety of conditions. Because it appeared that $\text{O}(^1\text{D})$ formation was a

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prerequisite to the successful reaction, several experiments were conducted using N_2O as the oxygen source:*



We were not only interested in an improved method for making ClF_3O but also in the formation of $FClO$. The latter could arise if the photolysis of $ClF-N_2O$ were rapid, thereby precluding marginally unstable materials from an excessive uv exposure.

Our experiments showed that ClF_3O is indeed formed during the photolysis of N_2O-ClF_3 , but no significant advantage over the O_2-ClF_3 reactant system was apparent. Further, despite a slight enhancement in rate of formation, it could not be conclusively established whether O fixation occurred as a result of O_2 dissociation or from the direct decomposition of N_2O to $O(^1D)$. It was noted that the reaction mixture was considerably more complex in that the fluorides FNO_2 and FNO were formed.

*We wish to thank Dr. A. Gordon, Naval Weapons Center, China Lake, Calif. for calling our attention to the fact that N_2O can give $O(^1D)$ with medium pressure lamps and for suggesting N_2O as an intermediate for ClF_3O synthesis.

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EXPERIMENTAL

FLUORINATION OF CHLORINE PERCHLORATE

A prepassivated 30-ml stainless-steel bomb was loaded with ClOClO_3 (53.1 cm^3 , 2.37 mmol) and approximately 1 liter of F_2 at -196°C . After 3 days at 0°C , the bomb was recooled to -196°C and the excess F_2 removed. The products were separated by fractional condensation and identified by their infrared spectra. In decreasing amount these were FClO_3 , ClF , and FClO_2 . Lesser quantities of SO_2F_2 and SF_6 (impurities in the F_2 supply) were also noted. No unreacted ClOClO_3 was recovered.

REACTION OF CHLORINE PERCHLORATE WITH CTF

Chlorine perchlorate (26.6 cm^3 , 1.19 mmol) and ClF_3 (25.9 cm^3 , 1.16 mmol) were condensed in a Teflon U-trap at -196°C . The reaction was allowed to proceed by warming the trap to 0°C for approximately 3 hours. Recooling to -196°C revealed only a trace of noncondensable gases had formed. Fractionation of the products through U-traps cooled to -78 , -112 , and -196°C indicated very minor amounts of ClOClO_3 and ClF_3 ($\sim 1 \text{ cm}^3$ each) remained unreacted. The products found were FClO_3 (22.9 cm^3 , 1.04 mmol), FClO_2 (14.7 cm^3 , 0.65 mmol), and ClF (32.9 cm^3 , 1.47 mmol).

ATTEMPTED PREPARATION OF CHLORINE CHLORATE

A 1.5-g (12.2 mmol) sample of KClO_3 was loaded into a 30-ml stainless-steel cylinder in the dry box. Chlorine fluorosulfate (106.8 cm^3 , 4.76 mmol) was condensed into the cylinder at -196°C which was then left at -45°C for 19 days. On recooling to -196°C , some noncondensable gases were found ($\sim 10 \text{ cm}^3$ but not measured exactly). Vacuum fractionation was used to separate the other materials which were identified as ClO_2 (112 cm^3 , 5.00 mmol), Cl_2 (46.5 cm^3 , 2.07 mmol) and perhaps a trace of Cl_2O_6 .

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PREPARATION OF NITRYL CHLORIDE

In a typical experiment calcium hypochlorite (2.34 g, 16 mmol, 95 percent, Research Inorganics Chemical Co.) was loaded into a 30-ml Hale stainless-steel cylinder in a drybox. After the cylinder was evacuated, FNO (3.75 mmol, prepared by reaction of F_2 with NO) was condensed in at -196 C . The sample was then warmed to a reaction temperature of -126 C . A reaction time of 1 hour was found to be sufficient. After reaction, volatile products were condensed at -196 C and separated by fractional condensation through traps held at -95 , -126 , -142 , and -196 C . Small amounts of HNO_3 (0.10 mmol) were found at -95 C , $ClNO_2$ (2.93 mmol, 78-percent yield based on FNO) was condensed at -126 and -142 C , and Cl_2 (0.07 mmol) at -142 C .

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APPENDIX A

CHLORINE PERCHLORATE

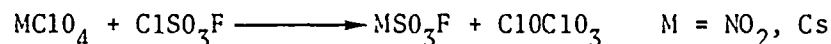
by Carl J. Schack and Don Pilipovich

Contribution from Rocketdyne,
a Division of North American Rockwell Corporation,
Canoga Park, California 91304

Abstract

The new chlorine oxide, ClOClO_3 , has been prepared in high yield by the reaction of either cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate at -45° . Characteristic physical data are reported for the compound together with some of its chemical reactions. Chlorine monofluoride also reacts with perchlorates to form ClOClO_3 but in low yield.

Halogen fluorosulfates and peroxydisulfuryl difluoride have been shown to be effective in oxidizing a variety of anions¹⁻³ or in displacing halogen substituents from certain covalent species⁴. For example, ClSO_3F can react³ with AgCl to generate Cl_2 or with CsF to generate ClF and the respective metal fluorosulfate. The present investigation sought to take advantage of this type of interaction using perchlorate salts as the anionic substrates. It has been found that this reaction results in the formation of the new chlorine oxide, chlorine perchlorate.



These reactions occur in high yield (75-95%) over a period of several days or less at approximately -45° .

Experimental

Apparatus and Materials. The equipment used in this work has been described³ and was supplemented with a Perkin-Elmer Infracord, Model 457. Cesium perchlorate (Matheson, Coleman and Bell) and nitronium perchlorate

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(Callery Chemical Co.) were purchased and used without further purification. Chlorine fluorosulfate was prepared from ClF and SO_3 as reported previously³. Gaseous reactants were purified by fractional condensation. All handling of solids was performed in a dry-nitrogen filled glove box. As a routine operation, all metal or Teflon equipment was passivated with ClF_3 before use.

Preparation of ClOClO_3 . In a typical experiment, a 30 ml stainless-steel cylinder was loaded with 2.45 g (10.5 mmol) of CsClO_4 . After evacuation, ClSO_3F (218 cm^3 , 9.73 mmol) was condensed into the cylinder at -196° . The reaction was allowed to proceed by maintaining the cylinder at approximately -45° for several days. The products were separated by fractional condensation in U traps cooled to -78° , -112° , and -196° . Little or no gases not condensable at -196° were found. The -196° fraction (8.0 cm^3 , 0.36 mmol) was primarily Cl_2 with a small amount of SO_2F_2 , while the -78° fraction was negligibly small. Pure ClOClO_3 (207 cm^3 , 9.24 mmol) was retained at -112° . The yield was 95%. A similar reaction using NO_2ClO_4 (2.0 g, 13.7 mmol) and ClSO_3F (200 cm^3 , 8.93 mmol) produced ClOClO_3 (170 cm^3 , 7.59 mmol) in 82% yield. The solid products from these reactions were identified as $\text{CsSO}_3\text{F-CsClO}_4$ and $\text{NO}_2\text{SO}_3\text{F-NO}_2\text{ClO}_4$ mixtures by their infrared spectra⁵⁻⁷. Synthetic reactions of this scale with either salt when terminated after 3-4 days were found to be complete with no detectable ClSO_3F remaining. Normally, longer reaction times were used to ensure complete consumption of ClSO_3F since its vapor pressure and that of ClOClO_3 are much too close to allow separation by a fractionation procedure. For the same reason, all preparations were conducted with excess perchlorate salt.

Properties of ClOClO_3 . Chlorine perchlorate is a pale yellow liquid and nearly white when frozen. It is stable for limited periods at room temperature in clean, dry, prepassivated stainless steel or perhalogenated plastic equipment. Storage at -45° in stainless-steel cylinders has resulted in <1% decomposition per week over a twelve week period. Products of this low-temperature decomposition are Cl_2 , O_2 and Cl_2O_6 which are readily separated from ClOClO_3 .

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Analysis. Thermal decomposition of ClOClO_3 (91.0 cm^3 , 4.06 mmol) in a stainless-steel cylinder for 3 days at ambient temperature followed by 18 hours at 150° resulted in complete degradation to the elements: Cl_2 (90.8 cm^3 , 4.05 mmol) identified by vapor pressure and gas chromatography and O_2 (181.0 cm^3 , 8.08 mmol) identified by vapor pressure and mass spectroscopy. Therefore, the observed ratio of $\text{Cl}_2:\text{O}_2$ was 1.00:1.99 compared to the theoretical ratio of 1.00:2.00.

Molecular Weight. Values for the molecular weight of ClOClO_3 as determined by gas density, assuming ideal gas behavior, were 133, 135, 134 (calc 135).

Vapor Pressure and Boiling Point. The vapor pressure of ClOClO_3 over the temperature range -47° to 21° is $[t (^\circ\text{C}), P(\text{mm})]$: $-46.8, 8$; $-31.3, 21$; $-24.2, 32$; $0.0, 119$; $5.0, 150$; $11.2, 202$; $18.9, 283$; $20.9, 305$. The vapor pressure-temperature relationship is described by the equation $\log P_{\text{mm}} = 7.8156 - 1568.0/T^\circ\text{K}$. The normal boiling point calculated from the equation is 44.5° , with a heat of vaporization of 7.17 kcal/mole and a Trouton constant of 22.6.

Melting Point. Samples of ClOClO_3 frozen as a ring in the upper part of a Teflon tube were observed to melt at $-117 \pm 2^\circ$.

Density. The densities measured in a Pyrex pycnometer at -78.8 , 0.0 , and 21.2° were 1.98, 1.82, and 1.75 g/ml . Over this temperature range the density ρ is given by the equation: $\rho = 1.806 - 2.30 \times 10^{-3} t^\circ\text{C}$.

Infrared Spectrum. The infrared spectrum was recorded in stainless steel or Kel-F cells fitted with AgCl windows over the range $4000\text{-}400 \text{ cm}^{-1}$ at a variety of pressures. Spectra are shown in Figure 1 at two pressures. The principal bands observed are: 1282 (vs) , 1041 (s) , 752 (w) , 661 (sh) , 652 (s) , 585 (sh) , 574 (sh) , 561 (m) and $511 \text{ (w)} \text{ cm}^{-1}$.

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Reactions of ClOClO_3 . Hydrogen Chloride. A Pyrex ampoule was loaded with ClOClO_3 (36.2 cm^3 , 1.62 mmol) and HCl (42.6 cm^3 , 1.90 mmol) at -196° . After maintaining the ampoule at -78° for 1 hour, separation of the products was initiated by first pumping the -78° volatiles through U traps cooled to -142° and -196° and later changing the ampoule to -45° while continuing to pump through the cold traps. The -196° trap contained unreacted HCl (6.0 cm^3 , 0.27 mmol) while the -142° trap contained only Cl_2 (36.4 cm^3 , 1.62 mmol). After warming the ampoule to room temperature, the weight of material retained at -45° was determined and this material transferred to the vacuum line. It was identified as HClO_4 (0.155 g, 1.54 mmol) by its vapor pressure⁸ and infrared spectrum⁹.

Reaction With AgCl . A sample of ClOClO_3 (7.9 cm^3 , 0.35 mmol) was loaded in a Kel-F infrared cell fitted with AgCl windows. On standing at ambient temperature for several hours, the ClOClO_3 was consumed leaving a thin deposit on the windows which was identified as ClO_4^- by its infrared spectrum⁵. No other infrared absorbing material was detected. After a day, the contents of the cell were analyzed by gas chromatography and found to be pure Cl_2 (7.5 cm^3 , 0.33 mmol).

Decomposition in Pyrex. Chlorine perchlorate (42.6 cm^3 , 1.90 mmol) was condensed into a 150 cm^3 Pyrex bulb (equipped with a Fischer-Porter Teflon needle valve and a metal-to-glass seal to eliminate greased closures or connections) at -196° . The bulb was allowed to warm to room temperature in a closed, dark, steel can and to stand for several days. At this time, the bulb was observed to contain a small puddle of a red, somewhat viscous liquid. The contents were rapidly vacuum fractionated through traps cooled to -78° , -112° , and -196° . An unmeasured but appreciable amount of gas not condensable at -196° was observed. The other volatile products were Cl_2 (19.0 cm^3 , 0.85 mmol), ClO_2 (9.9 cm^3 , 0.44 mmol), and ClOClO_3 ($\sim 1 \text{ cm}^3$) as identified by their vapor pressure and/or infrared spectra. The red liquid was not readily pumped out of the bulb and exhibited a low (1-2 mm) vapor pressure at ambient temperature. On standing at ambient temperature, the liquid slowly generated Cl_2 , ClO_2 and

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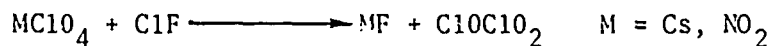
noncondensable gases. From these observations the liquid was identified as Cl_2O_6 .¹⁰ Based on 1 Cl_2O_6 from 2ClOClO_3 , the Cl_2O_6 yield was approximately 80%.

A similar experiment in which the Pyrex bulb was of much smaller volume ($\sim 20 \text{ cm}^3$) was examined after 2 days. The charged ClOClO_3 (53.5 cm^3 , 2.39 mmol) was completely decomposed giving much O_2 , Cl_2 (41.0 cm^3 , 1.83 mmol), and ClO_2 (18.6 cm^3 , 0.83 mmol). Only a small droplet of the red, liquid Cl_2O_6 was observed which, considering the chlorine evolved as Cl_2 and ClO_2 , could not have amounted to >12% yield.

Photolysis. Chlorine perchlorate (35.3 cm^3 , 1.58 mmol) was condensed into a 200 cm^3 quartz bulb at -196° . The bulb was warmed to room temperature and irradiated with uv light overnight (Hanovia 100 W Utility Lamp, Cat. No. 30620). After recooling to -196° , the noncondensable gases were measured (32.8 cm^3 , 1.46 mmol) and identified as O_2 by mass spectroscopy. Fractional condensation of the remaining material at -78° and -196° gave Cl_2 (24.8 cm^3 , 1.11 mmol) and Cl_2O_7 (10.2 cm^3 , 0.46 mmol) as the only detectable products. Chlorine heptoxide was identified by its vapor pressure and infrared spectrum.¹¹ Based on 1 Cl_2O_7 from 2ClOClO_3 , the yield was 58%.

Results and Discussion

Four reasonably stable oxides of chlorine are known and have been well characterized:¹² Cl_2O , ClO_2 , Cl_2O_6 , and Cl_2O_7 . More recently, a fifth compound of very limited stability has been reported¹³ with the empirical formula $\text{ClO}_{1.5}$ and the postulated composition OClClO_2 . The new chlorine oxide, ClOClO_3 , reported here was first obtained some time ago by the reaction of ClF and perchlorate salts at -78° or -45° .



However, the yields from these reactions were low ($\sim 5\%$) and somewhat irreproducible allowing only a tentative identification based on infrared data. The discovery of the present high yield synthesis confirmed the nature this low yield product and facilitated its characterization.

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Caution. While no incidents were encountered during this work, chlorine perchlorate should be treated with all safety precautions appropriate to the use of any chlorine oxide. It is shock sensitive.¹⁴

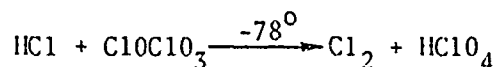
Chlorine perchlorate has been identified by its vapor density, elemental analysis, and infrared spectrum. A stable mass cracking pattern was not obtained but prominent m/e peaks for ClO_3^+ , ClO_2^+ , and ClO^+ were found. The absence of a parent ion peak is not surprising in view of its near absence in the reported¹⁵ mass spectrum of Cl_2O_7 for example. The basic physical and chemical properties have been determined and all data are consistent with the formulation ClOClO_3 .

Alternate structural formulations for the compound were ruled out on the basis of the infrared spectrum, Figure 1, and the chemical reactions discussed later. The strong bands at 1282 and 1041 cm^{-1} are readily assignable to the ClO_3 antisymmetric and symmetric stretching vibrations. The position, shape, and relative intensity of these two bands are remarkably similar to those of HOClO_3 ⁹ (1263 and 1050 cm^{-1}), $\text{O}_3\text{ClOClO}_3$ ¹¹ (1309 and 1025 cm^{-1}), and FOClO_3 ¹⁶ (1298 and 1049 cm^{-1}) and thus are indicative of a covalent perchlorate group. Furthermore, the exact position of the strongest observed ClO_3 antisymmetric stretching vibration correlates well with the electronegativity of the attached group. For the series of XClO_3 compounds, where X is F-, O_3ClO -, FO-, HO-, this band is located respectively at 1315, 1309, 1298, and 1263 cm^{-1} . The position of this band for chlorine perchlorate (1282 cm^{-1}) is compatible with this correlation, further supporting the assigned structural formula. Other noteworthy bands for ClOClO_3 are at 752 and 652 cm^{-1} . These bands are assignable to stretching modes of the Cl-O-Cl link. Comparable terminal Cl-O absorptions are found at 720 and 703 cm^{-1} for SF_5OCl ¹⁷ and ClOSO_2F ¹⁸ while FOClO_3 has a strong band at 666 cm^{-1} which has been ascribed¹⁵ to its singly bonded chlorine-oxygen stretching vibration. A detailed analysis of the vibrational spectrum of ClOClO_3 is in progress.¹⁹

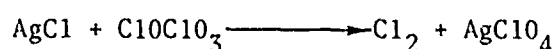
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Reaction of ClOClO_3 and HCl occurred rapidly and nearly quantitatively.



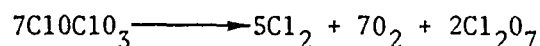
However, with AgCl large variations in the reaction rate were noted although the same final result was reached.



Several factors including the surface state of the AgCl and trace impurities in the ClOClO_3 may account for this. In general this reaction was slower than the corresponding $\text{AgCl}-\text{ClSO}_3\text{F}$ reaction³. The products from both of these chloride reactions conclusively support the postulated perchlorate structure derived from infrared data.

The thermal stability of ClOClO_3 at ambient temperature is limited with either glass or stainless-steel containers. A preparation conducted at ambient temperature in stainless steel gave no ClOClO_3 but a nearly quantitative yield of its elemental decomposition products. Pure ClOClO_3 also decomposed readily in Pyrex in the absence of light. Yields of the products of this decomposition differed greatly with the container volume and may have been influenced by other unknown variables, but a high conversion to Cl_2O_6 (80%) was possible. The only other chlorine oxide found was ClO_2 , the other products being Cl_2 and O_2 . The preparation of Cl_2O_6 by the thermal decomposition of ClOClO_3 may be an attractive alternate to the presently used photolysis of ClO_2 and O_3 .¹²

Irradiation of ClOClO_3 in quartz at ambient temperature produced Cl_2O_7 in a reaction approximating the stoichiometry:



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Formation of Cl_2O_7 directly by recombination of ClO_4 and ClO_3 radicals generated from ClOClO_3 is possible. But Cl_2O_7 can also result²⁰ from irradiation of Cl_2O_6 , which as noted above can be formed from ClOClO_3 .

The overall stability of ClOClO_3 approaches that of the four well known chlorine oxides and is quite unlike that of the analogous compound FOClO_3 which tends to explode on freezing or during other simple operations.²¹ This behavior trend is comparable to that of FONO_2 ²² vs ClONO_2 ²³. However, it is the opposite of the general stability found^{17,24-26} for highly fluorinated FO- and ClO- substituted compounds, CF_3OF vs CF_3OCl or SF_5OF vs SF_5OCl , where the ClO- derivatives are less stable.

Using the known heats of formation (kcal/mole) of FOClO_3 ²⁷ (+37.6) and those of the related pairs of compounds, OF_2 ²⁸ (+5.5) - Cl_2O ²⁹ (+21.0) and FONO_2 ²⁷ (+2.5) - ClONO_2 ³⁰ (+7.0), the heat of formation of ClOClO_3 was estimated as approximately +43. This value is reasonable, in view of the heats of formation of ClO ²⁹ (+24) and ClO_3 ²⁸ (+37), since the formation of the ClO- ClO_3 bond should be somewhat exothermic.

Acknowledgement. The authors wish to acknowledge sincere appreciation for support of this work by the Office of Naval Research, Power Branch. We also thank Dr. K. O. Criste for helpful discussions.

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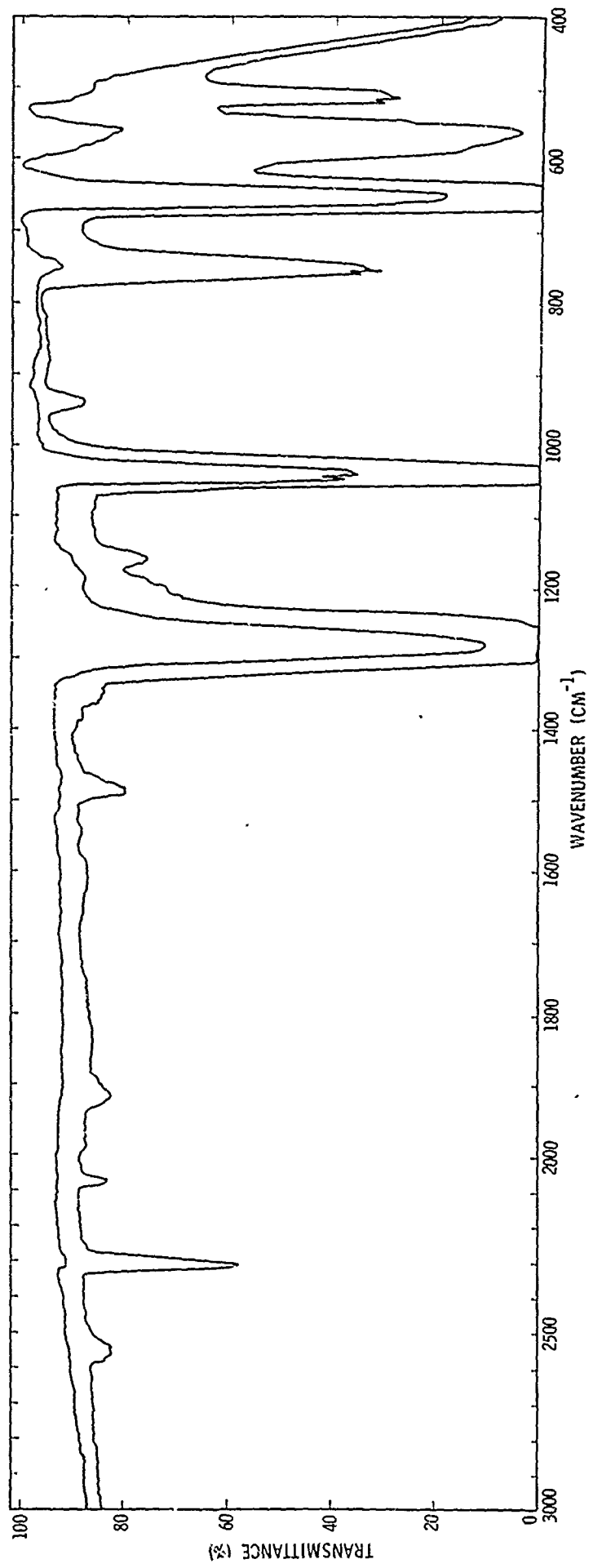


Figure 1. Infrared Spectrum of ClOClO₃ at 180 and 8 mm, 5 cm Path

APPENDIX B

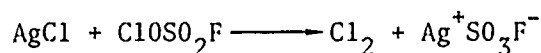
INFRARED SPECTRUM OF ClOSO_2F

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Abstract. The infrared spectra of gaseous and solid ClOSO_2F have been measured. Ten of the 12 fundamentals were observed and a vibrational assignment for symmetry C_s is suggested. Some thermodynamic properties and principal force constants have been computed.

Introduction

Chlorine fluorosulfate, ClOSO_2F , was first reported by Gilbreath and Cady [1] in 1963. However, no infrared data have been reported for this interesting compound. Recently, one of us [2] has found that ClOSO_2F can be conveniently prepared by the addition of ClF to SO_3 . Furthermore, it was found that ClOSO_2F rapidly attacks conventional infrared windows such as NaCl or AgCl according to:



This instantaneous attack on the windows explains the absence of infrared data in previous reports on chlorine fluorosulfate. It was also noted that this attack is catalyzed by trace impurities, possibly HF , but that carefully purified ClOSO_2F shows practically no attack on the windows. In this paper we wish to report the infrared spectrum of gaseous and solid ClOSO_2F and its assignment for symmetry C_s .

Experimental

The preparation, purification, and handling of ClOSO_2F has been described elsewhere [2]. The infrared spectra of gaseous and solid ClOSO_2F were recorded on a Beckman Model IR-7 (with CsI interchange) and Perkin Elmer Models 337 and 457 spectrophotometers in the ranges 700-250, 4000-400, and 4000-250 cm^{-1} , respectively. The instruments were calibrated by comparison with standard calibration points [3]. The spectrum of the gas was obtained using a 304 stainless-steel cell of 5-cm path length fitted with AgCl windows. The low-temperature spectrum of the solid was recorded by condensing the compound on the internal cold (-196°) window of a conventional low-temperature cell. The body of this cell was made from Pyrex glass, all windows being either AgCl or CsI.

Results and Discussion

Figure 1 shows the infrared spectrum of gaseous ClOSO_2F at two different pressures. Figure 2 shows the infrared spectrum of solid ClOSO_2F at three different concentrations. Table I lists the observed frequencies together with their assignment for pointgroup C_s . For comparison, the vibrational frequencies of similar molecules are also given. Pointgroup C_s , having a symmetry plane, was preferred over pointgroup C_1 , having no symmetry element. This preference was based on the assumption that the F, Cl, and O ligands are all of relatively high electronegativity and hence will repel each other. Because the chlorine atom should be repelled most strongly by the most electronegative ligand, it was assumed to be located in a trans-position to the fluorine atom, thus creating a symmetry plane. However, the barrier to internal rotation is expected to be quite low. Consequently, ClOSO_2F might show hindered rotation only at relatively low temperature.

For a six atomic molecule of symmetry C_s (or of no symmetry), a total of 12 fundamental vibrations is expected. By comparison with the known spectrum of ClONO_2 [4], one would expect the SOCl deformation and SOCl

Table I. Infrared Spectrum of ClOSO_2F (cm^{-1}) compared to those of related molecules

| ClOSO_2F | | Approximate Description of Vibration | FSO_2F [5] | FOSO_2F [6] | $\text{F}_2\text{NOSO}_2\text{F}$ [7,8] | HOSO_2F [9,10] | $\text{CH}_3\text{OSO}_2\text{F}$ [6] | ClOSO_2F [11] |
|--------------------------|----------------|--|-------------------------------|--------------------------------|--|-----------------------------------|--|----------------------------------|
| Gas | Solid | | | | | | | |
| 2960vvw | | $2\nu_9 = 2962$ | | | 2990vvw | | | |
| 2725vw | | $\nu_1 + \nu_9 = 2729$ | | | 2748vw | | | |
| 2498vw | | $2\nu_1 = 2496$ | | | 2500vvw | | | |
| 1704vvw | | $2\nu_2 = 1710$ | | | 1681vw | | | |
| 1665vw | | $2\nu_3 = 1662, \nu_2 + \nu_3 = 1686$ | | | 1560vw | | | |
| 1550vw | | $\nu_3 + \nu_4 = 1546$ | | | 1540vw | | | |
| 1481vs | 1458vs | $\nu_9(\text{A}'') \text{ SO}_2 \text{ asym. stretch}$ | 1502 | 1501 | 1493 | 1480 | 1465 | |
| 1248vs | 1238vs | $\nu_1(\text{A}') \text{ SO}_2 \text{ sym. stretch}$ | 1269 | 1248 | 1254 | 1243 | 1235 | |
| 1035vw | | $\nu_2 + \nu_8 (?)$ | | | | | | |
| 855vs | 876s | $\nu_2(\text{A}') \text{ SF stretch}$ | 885 848 | 852 | 842 | 896 | 840 | |
| 831ms, sh | 837ms | $\nu_3(\text{A}') \text{ SO stretch}$ | -- | 789 | 779 | 955 | 787 | 830 |
| 703ms | 709ms | $\nu_4(\text{A}') \text{ OCl stretch}$ | -- | -- | -- | -- | -- | 720 |
| 620vw | | | | | | | | |
| 572ms | 573ms 545vw | $\nu_5(\text{A}') \text{ SO}_2 \text{ bend}$ | 544 | 575 | 543 | 556 | 575 | |
| 529m | 532m | $\nu_{10}(\text{A}'') \text{ SO}_2 \text{ rock}$ | 553 | 520 | 543 | 556 | 520 | |
| 486mw | 487mw | $\nu_6(\text{A}') \text{ SO wag}$ | -- | | 485 | 409 | | |
| | 390w | $\nu_{11}(\text{A}'') \text{ SO}_2 \text{ torsion}$ | 388 | | | 390 | | |
| | 364mw | $\nu_7(\text{A}') \text{ SF wag}$ | 384 | | | 390 | | |

torsion vibration in ClOSO_2F to occur below 250 cm^{-1} . Hence, for ClOSO_2F we should expect 10 fundamental vibrations in the range $4000\text{--}250\text{ cm}^{-1}$. As can be seen from Table 1, the correct number of 10 fundamentals has been observed, their frequencies and intensities being in good agreement with those reported for similar molecules [5-11]. The low-temperature infrared spectrum of solid ClOSO_2F has also been recorded to better resolve the two bands at about 850 cm^{-1} , which overlap in the gas phase, and to avoid attack on the CsI windows. The agreement between the spectrum of the gas and that of the solid is relatively good indicating little or no association in the solid state.

The assignment of the fundamental vibrations of ClOSO_2F was made by analogy with those reported for related compounds [5-11]. Some additional support for the listed assignments can be obtained from the band shapes in the gas spectrum. Thus, the band at 572 cm^{-1} exhibits a PQR structure and hence should be assigned to $\nu_5 (\text{A}')$. Furthermore, the bands at 1248, 855, and 831 cm^{-1} have a shape closer to that expected for parallel bands, whereas the 1481, 703, and 520 cm^{-1} bands more closely resemble perpendicular bands.

The frequencies of the two SO_2 stretching vibrations show a slight dependence on the electronegativity of the O-X substituent. As in the case of P=O , C=O , or Cl=O bonds the SO_2 frequencies increase with increasing electronegativity of the remaining substituents [12]. The infrared spectrum of gaseous and solid $\text{NF}_2\text{OSO}_2\text{F}$ has also been recorded [8] in the range $4000\text{--}250\text{ cm}^{-1}$ and showed in addition to the bands listed in Table I absorptions (in cm^{-1}) at 658 w, 620 s (PQR), 425 m, 341 w, and 321 mw; which had previously [7] not been reported.

A normal coordinate analysis was made for this molecule using the reparameterization method [13], assuming the geometry to be similar to that of related molecules and using the assignments given above. There are 51 force constants in the general valence field, and little is known about the force constants of this type of molecule. Hence, additional data would be required for computing unique force constants. However, the stretching

force constants were found to be quite independent of the interaction constants and therefore should be meaningful. The computed values for the principal force constants are: $f_{S=O} = 10.9$, $f_{S-F} = 4.4$, $f_{S-O} = 3.8$, and $f_{O-C1} = 2.6$ mdynes/ $\overset{O}{\text{Å}}$. Because the bending force constants strongly depend on the interaction constants their values are not reported. To exactly fit the force constants to the observed frequencies, a number of interaction constants of appreciable value were required. This indicates that some of the deformation vibrations for this class of compounds may have to be reassigned. Therefore, the normal coordinate analysis adds little further credibility to the assignment and its validity rests mainly on the arguments given above.

The thermodynamic properties were computed for this molecule using the rigid-rotor-harmonic-oscillator approximation [14]. The results are given in Table II. The frequencies used are those of Table 2 and the moments of inertia used are 505, 492, and 153×10^{-40} g-cm². Free rotation was assumed (which introduces very little error if the mode is below 100 cm⁻¹) and the reduced moment of inertia was taken as 77×10^{-40} g-cm².

Acknowledgement. We are indebted to Mr. W. H. Moberly for computing the thermodynamic properties and to Dr. D. Pilipovich for continuous encouragement. This work was supported in part by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force under Contract AF49(638)-1734.

Table II. Thermodynamic Properties of ClOSO_2F assuming an ideal gas at 1 atmosphere pressure; units for C_p^0 , S^0 , and $-(F^0 - H_0^0)/T$ are calories per mole-degree and H_0^0 is kilocalories per mole.

| T, °K | C_p^0 | $(H^0 - H_0^0)$ | $-(F^0 - H_0^0)/T$ | S^0 |
|--------|---------|-----------------|--------------------|---------|
| 0 | 0 | 0 | 0 | 0 |
| 100 | 10.826 | 0.948 | 57.461 | 66.944 |
| 200 | 15.617 | 2.266 | 64.555 | 75.884 |
| 298.15 | 19.652 | 4.007 | 69.474 | 82.914 |
| 300 | 19.716 | 4.043 | 69.558 | 83.035 |
| 400 | 22.605 | 6.168 | 73.707 | 89.128 |
| 500 | 24.613 | 8.535 | 77.331 | 94.402 |
| 600 | 26.024 | 11.071 | 80.569 | 99.021 |
| 700 | 27.033 | 13.727 | 83.504 | 103.112 |
| 800 | 27.770 | 16.469 | 86.187 | 106.773 |
| 900 | 28.319 | 19.274 | 88.661 | 110.077 |
| 1000 | 28.737 | 22.128 | 90.955 | 113.082 |
| 1100 | 29.060 | 25.018 | 93.094 | 115.837 |
| 1200 | 29.316 | 27.937 | 95.096 | 118.378 |
| 1300 | 29.520 | 30.880 | 96.979 | 120.732 |
| 1400 | 29.685 | 33.840 | 98.754 | 122.926 |
| 1500 | 29.821 | 36.815 | 100.435 | 124.978 |
| 1600 | 29.934 | 39.804 | 102.030 | 126.908 |
| 1700 | 30.029 | 42.802 | 103.547 | 128.725 |
| 1800 | 30.110 | 45.808 | 104.994 | 130.444 |
| 1900 | 30.178 | 48.823 | 106.377 | 132.073 |
| 2000 | 30.237 | 51.844 | 107.701 | 133.623 |

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* This work was supported by the Office of Naval Research, Power Branch.

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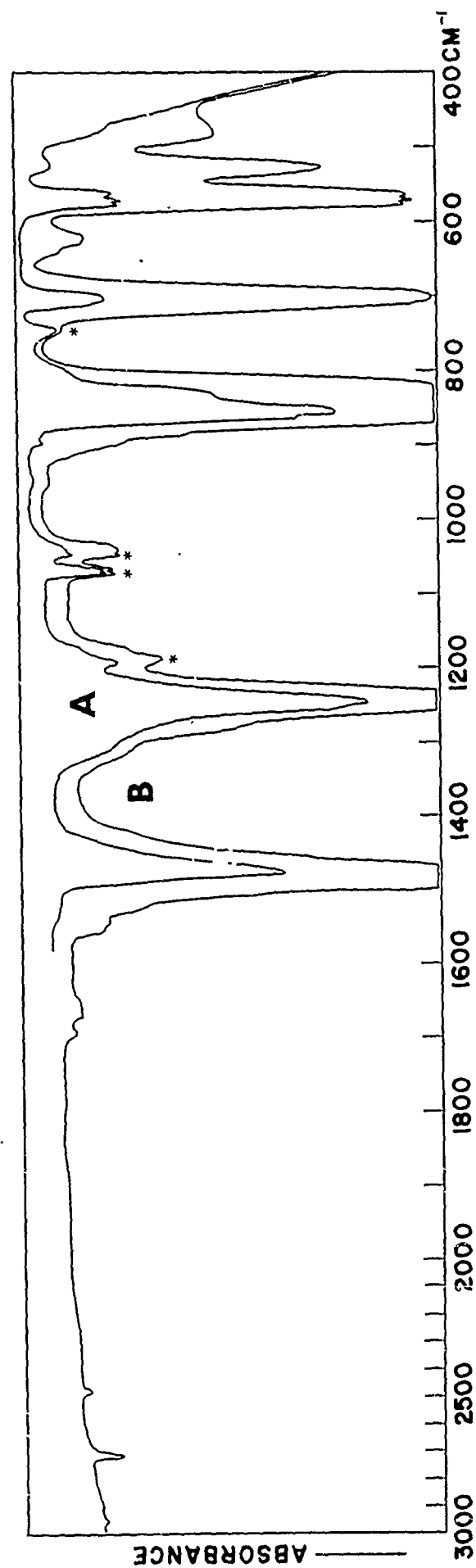


Figure 1. Infrared Spectrum of gaseous ClO_2F .

A:P = 8 mm Hg, B:P = 30 mm Hg, Bands marked with an asterisk are probably due to background

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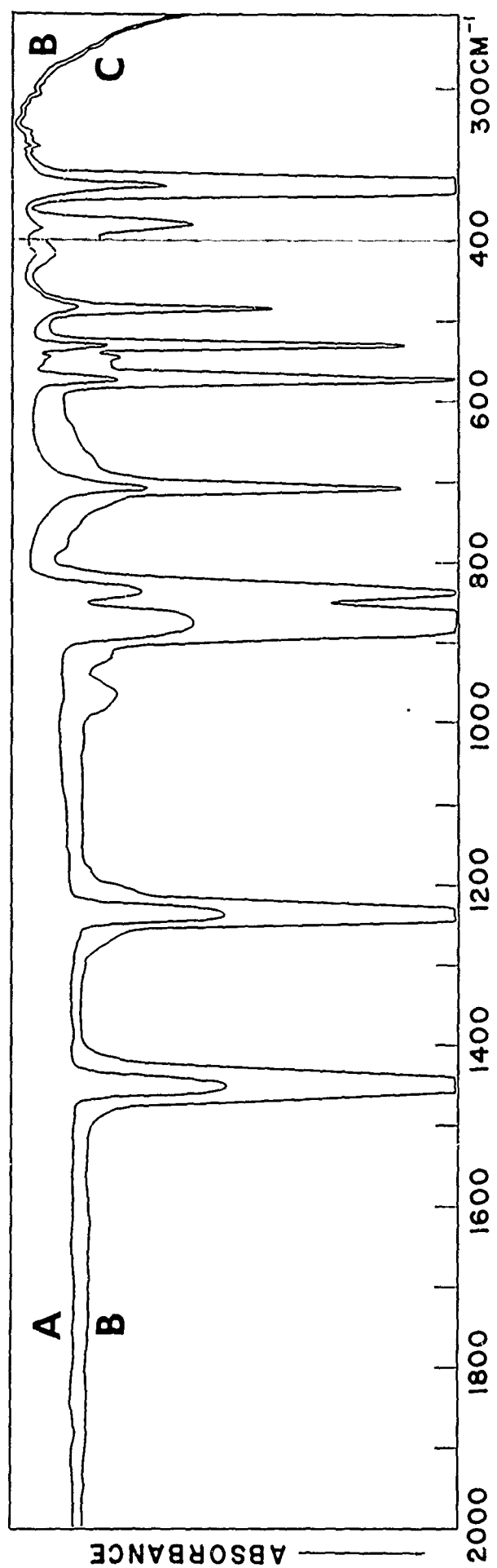


Figure 2. Infrared spectrum of solid ClOSO_2F at three different concentrations.

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Security Classification

| DOCUMENT CONTROL DATA - R & D | | |
|---|--|--|
| (Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified) | | |
| 1. ORIGINATING ACTIVITY (Corporate author) Rocketdyne, a Division of North American Rockwell Corporation, 6633 Canoga Avenue, Canoga Park, California 91304 | | 2a. REPORT SECURITY CLASSIFICATION CONFIDENTIAL |
| | | 2b. GROUP 4 |
| 3. REPORT TITLE INORGANIC HALOGEN OXIDIZERS | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Semiannual Report, 1 April 1969 through 30 September 1969 | | |
| 5. AUTHOR(S) (First name, middle initial, last name) Pilipovich, D.; Christe, K. O.; Schack, C. J.; Wilson, R.D.; Lindahl, C. B.; Curtis, E. C. | | |
| 6. REPORT DATE 31 October 1969 | 7a. TOTAL NO. OF PAGES 40 | 7b. NO. OF REFS 8 |
| 8a. CONTRACT OR GRANT NO. Nonr 4428(00) | 9a. ORIGINATOR'S REPORT NUMBER(S) R-8037 | |
| b. PROJECT NO. | | |
| c. | | |
| d. | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| 10. DISTRIBUTION STATEMENT | | |
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY Office of Naval Research Power Branch, Code 429 Washington, D.C. | |
| 13. ABSTRACT The new compound chlorine perchlorate, Cl_2O_4 , was synthesized from the action of chlorine fluorosulfate on several perchlorate salts. Characterization data, physical and chemical properties are described. The use of N_2O as an oxygen source for the synthesis of ClF_3 was successful but offered no advantages over oxygen. A new synthesis of nitryl chloride emerged from the studies of $\text{Ca}(\text{OCl})_2$ as an intermediate and involved the action of nitrosyl fluoride, FNO , on calcium hypochlorite. A structural evaluation on chlorine fluorosulfate was carried out from its ir spectrum. C_s symmetry for ClSO_3F was suggested and thermodynamic properties and force constants were computed. (C) | | |

DD FORM 1 NOV 63 1473

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Security Classification

| 14 | KEY WORDS | LINK A | | LINK B | | LINK C | |
|----|--|--------|----|--------|----|--------|----|
| | | ROLE | WT | ROLE | WT | ROLE | WT |
| | Halogen Oxidizers Chlorine Oxyfluorides | | | | | | |

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